

Anionic Surfactants as Corrosion Inhibitors for Carbon Steel in HCl Solution

HARISH KUMAR* and SUNITA

*Department of Chemistry, Ch. Devi Lal University, Sirsa (Haryana), India

ABSTRACT

The role of some surfactants in the corrosion of carbon steel in 1.0 M HCl has been studied using weight loss and galvanostatic polarization techniques. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreased with increasing temperature which is due to the fact, that the rate of corrosion of carbon steel is higher than the rate of adsorption. The inhibiting action of these compounds are considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicate the joint adsorption of these compounds and iodide ions. Thermodynamic parameters for adsorption and activation processes were determined. Galvanostatic polarization data indicated that these compounds act as mixed-type inhibitors. Results obtained from the two techniques are in good agreement.

Keywords: Corrosion inhibitors, surfactant, Carbon Steel.

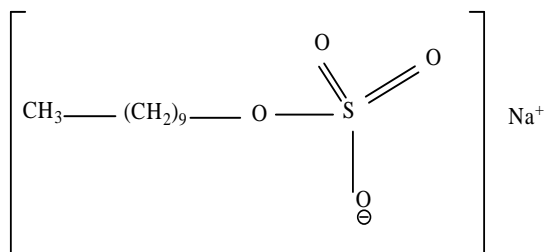
INTRODUCTION

Carbon steel has remarkable economic and attractive materials for engineering applications owing to its low cost, easy availability and high mechanical strength. The interest of the materials arises from their importance in recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type

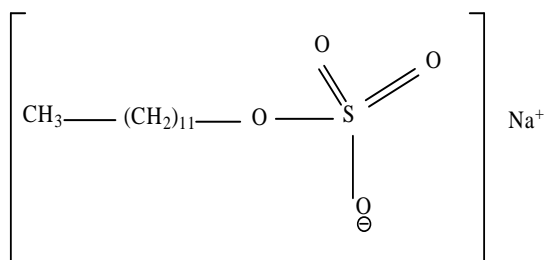
of corrosion media¹. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of metal dissolution in such solutions. Thus, many studies concerning the inhibition of carbon steel corrosion using organic substances are conducted in acidic and basic solutions²⁻⁶.

The present study aimed to investigate the efficiency of some surfactants as corrosion inhibitors for carbon steel in acidic media. An attempt was also made to clarify the effects of concentration and temperature on the inhibition efficiency of the studied surfactant as corrosion inhibitors for carbon steel. The measurements of corrosion rate and percentage inhibition

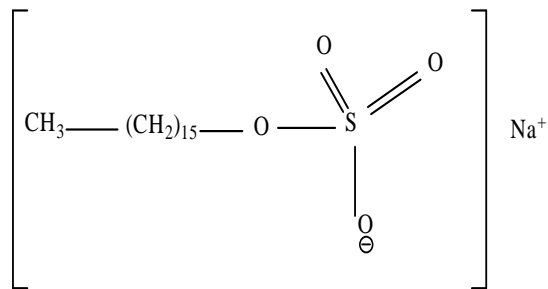
efficiency of different anionic surfactant towards corrosion of carbon steel by weight loss and electrochemical polarization technique were performed in 1.0 M HCl without and with the presence of the investigated surfactants in the concentration range (10 to 100 ppm). The name and molecular structures of the anionic surfactants as corrosion inhibitor for carbon steel in acidic medium are:



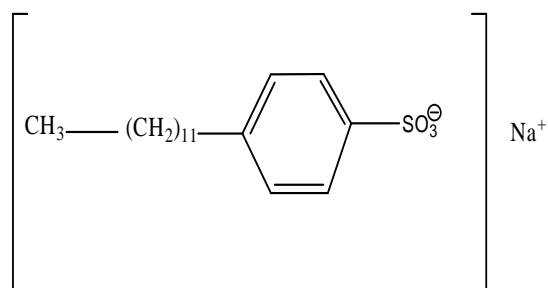
(a) Decyl sulphate sodium salt.



(b) - Dodecyl sulphate sodium salt.



(c) - Hexadecyl sulphate sodium salt.



(d) - Dodecyl benzene sulfonate.

EXPERIMENTAL

Carbon steel used for the investigations was in the form of sheet (0.25 mm thick) and had the following composition.

Element	C	Si	Mn	S	P	Ni	Cu	Cr	Fe
Weight percentage (w/w)	0.14	0.03	0.32	0.05	0.20	0.01	0.01	0.01	Balance

All the chemicals used were of AR grade and the solutions were prepared using triple distilled water. Duplicate or in some cases triplicate experiments have been performed to verify the reproducibility and consistency of the experimental data.

For weight loss measurements, carbon steel specimens of $3 \times 1.5 \text{ cm}^2$ size were cut from the carbon steel sheet whereas for electrochemical polarization investigations, specimens of size $5 \times 1.0 \text{ cm}^2$ were used. All the specimens were mechanically polished successively with the help of emery papers of

grades 100, 200, 300, 400 and 600 μ and then thoroughly cleaned with plenty of triple distilled water and then with acetone. The specimens were dried with hot air blower and stored in desiccators over silica gel.

After recording the initial weights of carbon steel specimens on a Mettler Toledo, Japan AB 135-S/FACT, single pan analytical balance, (with a precision of 0.01mg), they were immersed in tilted position in 250 ml beakers each having 200 ml of acidic solution as corroding medium with or without the inhibitor. Experiments were carried out in an electronically controlled air thermostat at 30, 40 and 50 $^{\circ}$ C with in an accuracy of $\pm 0.1^{\circ}$ C. After exposing the specimens for 24 hours, the specimens were taken out from the beaker and washed initially under the running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and dried with hot air blower and then weighed again. Corrosion rate in mils per year (mpy) and percentage inhibition efficiency were calculated using the following equations.

$$\text{Corrosion rate (mpy)} = \frac{534 \times W}{DAT} \quad (1)$$

Where

W = Weight loss (mg), D = Density of carbon steel (gm/cm 3), A = Area of specimen (sq. inch), T = Exposure time (hours).

The degree of surface coverage (θ) of the investigated surfactant compounds were calculated from the following equation:

$$\theta = \left[1 - \left(\frac{\Delta W_{Inh}}{\Delta W_{Free}} \right) \right] \quad (2)$$

Where, ΔW_{Free} and ΔW_{Inh} are weight losses of metal per unit area in absence and presence

of inhibitor at given time period and temperature, respectively.

Electrochemical polarization studies were carried out in 500 ml glass cell having three electrodes system assembly. Potentiostatic polarization of the working electrode was carried out by using a Potentiostat / Galvanostat PGS 201 T (Tacussel, France).

The working electrode was carbon steel under study, platinum electrode was used as counter electrode or an auxiliary electrode. All the potentials were measured against a pencil type luggin capillary saturated calomel electrode as reference electrode. A Luggin capillary filled with the test solution was used to connect the reference electrode with the cell. The tip of the Luggin capillary was kept very close to the working area of the electrode but without touching it in order to minimize the IR drop and this distance was kept constant during the whole study. Only 1 cm 2 area of specimen was used as working area and the rest of the area of the specimen was covered with a lacquer except the other tip of specimen which was used for making electrical connection. The specimen was left in the test solution until a constant open circuit potential (OCP) was attained.

Linear polarization resistance measurements were carried out potentiostatically by scanning through a potential range of 14 mV above and below the OCP value in steps of 2 mV. Experiments were carried out in absence and presence of inhibitors at their different concentrations at 30, 40 and 50 $^{\circ}$ C. The resulting current is plotted against the potential and slope of the line is measured.

The corrosion current, I_{corr} is related to the slope of the line by Stern-Geary equation.

$$\frac{\Delta E}{\Delta i} = \frac{\beta_a \times \beta_c}{2.303 I_{corr} (\beta_a + \beta_c)} \quad (3)$$

Where $\frac{\Delta E}{\Delta i}$ is the slope which is linear polarization resistance (R_p), β_a and β_c are anodic and cathodic Tafel slopes respectively and I_{corr} is the corrosion current density in $\mu A/cm^2$.

The anodic and cathodic Tafel slopes were measured after recording anodic and cathodic polarization curves of the specimen up to a maximum shift of ± 140 mV from OCP value in steps of 10 mV. Experiments were carried out in absence and presence of the inhibitor at their 10 to 100 ppm concentrations at 30, 40 and 50°C.

Rearranging the above equation:

$$I_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \times \frac{1}{R_p} \quad (4)$$

The corrosion current density I_{corr} , is related to the corrosion rate by the equation,

$$\text{Corrosion rate (C.R.)} \\ (\text{mpy}) = \frac{0.1288 \times I_{corr} \times E q. W t.}{D} \quad (5)$$

Where

Eq. Wt. = Gram equivalent weight of metal/alloy, D = Density of metal (gm/cm^3), I_{corr} = Corrosion current density ($\mu A/cm^2$).

The interaction of inhibitor molecules can be described by introducing of an parameter, S_θ , obtained from the surface coverage values (q) of the anion, cation and both. Aramiki and Hackerman⁹ calculated the synergism parameter, S_θ , using the following equation.

$$S_\theta = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \quad (6)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, θ_1 = surface coverage by anion, θ_2 = surface coverage by cation and θ'_{1+2} = measured surface coverage by both the anion and the cation, which may be attributed to competitive adsorption as can be seen from Table (3), S_θ values nearly equal to unity which suggests that the enhanced inhibition efficiencies caused by the addition of these anions to surfactants is due to mainly to the synergistic effect.

RESULTS AND DISCUSSION

It is observed from the Table 1 that the weight loss decreased, percentage inhibition efficiency increased and therefore the corrosion inhibition strengthened with increase in inhibitor concentration from 10 to 100 ppm. This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration. Thus, the surface is efficiently separated from the medium⁷⁻⁸. The linear variation of weight loss with time in uninhibited and inhibited 1.0 M HCl indicates the absence of insoluble surface films during corrosion. Table 1 shows that percentage corrosion inhibition efficiency increases with increase in inhibitor concentration. The percentage corrosion inhibition efficiency for different investigated anionic surfactants as corrosion inhibitor increases in the following order $a > b > c > d$.

Table 2 gives the values of %IE for different concentrations of investigated surfactant compounds and 10^{-2} M KI. The addition of KI improves the %age corrosion inhibition efficiency of the investigated compounds significantly. The synergistic effect between Investigated compounds and KI is due to interactions between chemisorbed I- and

organic compounds. The stabilization of adsorbed organic cations on the surface, which may be exhibited by electrostatic interactions with I⁻ ions, leads to higher surface coverage and greater corrosion inhibition.

Table 4 shows typical current-potential of carbon steel in 1 M HCl in the absence and presence of various concentrations of organic surfactant. Values of associated electrochemical parameters such as current density (*i*_{corr}), corrosion potential (*E*_{corr}), Tafel slopes, and corrosion inhibition efficiency (per cent) as function of compound d concentrations in 1 M HCl are given in *Table 4*. It is evident from this *Table* that the Tafel constants did not change significantly. It observed from the Tafel curves that the inhibitor was mixed type because they enhance the anodic and cathodic processes but the anode is more polarized when an external current was applied. Addition of surfactant compounds increased both cathodic and anodic over voltage and caused mainly parallel displacement to the more negative and positive respectively.

- The corrosion current density (*i*_{corr}) decreases with increasing the concentration of surfactant compounds, which indicates that the presence of these compounds retards the dissolution of carbon steel in 1M HCl and the degree of inhibition depends on the concentration.

- The values of corrosion potential (*E*_{corr}) values shifted to less negative values by increasing the concentration of surfactant compounds.

The effect of temperature on the corrosion behavior of carbon steel was studied by weight loss methods at various temperatures in the range 30-50°C in the absence and

presence of different concentrations of compound (d) in 1M HCl media. and %age corrosion inhibition efficiency of compound (d) is shown in *Table 5*. It is obvious from the table that %age corrosion inhibition efficiency increases with increasing the concentration of compound (d) and decreases with increasing the temperature. This indicated fact that the augmentation of temperature led to the reduction of the inhibitor adsorption and then the acceleration of the dissolution process⁹⁻¹³.

The calculated values of the apparent activation energy, E_a^* , activation enthalpies, ΔH^* and activation entropies, ΔS^* are given in *Table 6*. These values indicate that the presence of the additives increases the activation energy, E_a^* and the activation enthalpy ΔH^* , and decreases the activation entropy, ΔS^* for the corrosion process. The addition of inhibitors modified the values of E_a^* . This is may be attributed to the adsorption of inhibitors on carbon steel surface., and this adsorption make an energy barrier and this energy barrier of corrosion reaction increases as the concentration of the inhibitor is increased., and hence %age corrosion inhibition efficiency increases. This suggested that the process is activation controlled. Since, the activation energy value of 63.96 kJ mol⁻¹ (*Table 6*) for HCl-inhibitor systems support the fact that the inhibitors are physically adsorbed on carbon steel surface. This is in agreement with reports of Abiola *et. al*¹⁴, Ebenso *et. al*¹⁵, Ebenso¹⁶ and Barrow¹⁷. According to these reports, E_a^* due to chemical adsorption (>80 kJ mol⁻¹) is considerably larger than due to physical adsorption (<80 kJ mol⁻¹) the increase in the activation enthalpy (ΔH^*) in presence of the inhibitors implies that the

addition of the inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. The entropy of activation (ΔS^*) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step¹⁸⁻²⁰.

Mechanism of corrosion inhibition of all the four investigated organic surfactants can be explained on the basis of the molecular size

and the number of adsorption centers. Organic surfactant compound (d) should be the most effective inhibitors, inspite of it has two active adsorption centers. The highest inhibition efficiency of the compound (d) may be due to : (i) higher molecular size and (ii) benzene ring contributes p electrons to the adsorption centers and hence increases the electron density on the adsorption centers. Compounds $a < b < c$ in percentage corrosion inhibition efficiency and this agrees with their molecular size.

Table 1. Percentage corrosion inhibition efficiency at different concentrations of anionic surfactant for the corrosion of carbon steel after immersion in 1.0 M HCl at 30°C.

Conc. of surfactant (ppm)	Percentage corrosion inhibition efficiency of anionic surfactants			
	(a)	(b)	(c)	(d)
10	65.6	70.5	76.2	77.0
30	67.2	70.6	77.1	79.5
50	68.9	77.0	72.9	80.3
70	69.7	78.2	78.6	82.8
90	71.2	79.5	78.7	83.6
100	71.3	79.5	81.1	86.9

Table 2. Percentage corrosion inhibition efficiency at different concentrations of the four investigated surfactant (a to d) compounds with addition of 1.0×10^{-2} M KI for the corrosion of carbon steel after 24 hours of immersion in 1.0 M HCl at 30°C.

Conc. of surfactant (ppm)	Percentage corrosion inhibition efficiency of anionic surfactants			
	(a)	(b)	(c)	(d)
10	79.5	80.3	83.6	85.2
30	82.0	83.5	84.4	85.3
50	82.8	83.6	84.4	85.4
70	83.1	84.3	85.7	87.7
90	83.6	86.1	86.1	87.8
100	85.2	86.9	87.7	90.9

Table 3. Synergism parameter (S_θ) for different concentrations of investigated surfactant compounds (a to d) with addition of 1.0×10^{-2} M KI for the corrosion of carbon steel after 24 hours of immersion in 1.0 M HCl at 30°C.

Conc. of surfactant (ppm)	Synergism parameter (S_θ)			
	(a)	(b)	(c)	(d)
10	1.007	1.076	1.123	1.157
30	1.016	1.081	1.124	1.176
50	1.022	1.084	1.140	1.196
70	1.028	1.092	1.146	1.213
90	1.040	1.102	1.151	1.231
100	1.063	1.107	1.158	1.263

Table 4. The effect of concentrations of compound (d) on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), %age corrosion inhibition efficiency (%age CIE) and degree of surface coverage (q) for the corrosion of carbon steel in 1.0 M HCl at 30°C.

Conc. of surfactant (d) (ppm)	$-E_{\text{corr}}$, mV	i_{corr} , ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$ (mV/dec)	β_a (mV/dec)	q	%age CIE
Blank	942	62.0	217	89	-	-
10	938	39.0	207	112	0.782	78.2
30	937	36.8	209	114	0.807	80.7
50	936	34.1	211	116	0.815	81.5
70	935	31.2	212	118	0.839	83.9
90	934	30.3	214	120	0.848	84.8
100	933	26.6	215	123	0.881	88.1

Table 5. The effect of temperature on the corrosion inhibition efficiency of organic surfactant (d) at different concentrations.

Conc. of surfactant (d)(ppm)	30 ⁰ C	40 ⁰ C	50 ⁰ C
10	28	23	21
30	32	28	26
50	35	32	28
70	38	35	32
90	42	37	34
100	47	38	35

Table 6. Activation parameters of the corrosion of carbon steel in 1.0M HCl in absence and presence of different concentrations of compound (d).

Conc. of surfactant (d)	$E_a^* (kJmol^{-1})$	$\Delta H^* (kJmol^{-1})$	$-\Delta S^* (Jmol^{-1}K^{-1})$
10	58.48	56.22	163.22
30	62.22	59.54	158.44
50	62.85	60.29	155.05
70	63.12	61.49	153.05
90	63.55	62.32	151.35
100	63.96	62.96	150.30

CONCLUSIONS

- The investigated surfactant compounds act as corrosion inhibitors for the carbon steel in hydrochloric acid solution.
- Surfactant compounds adsorb on carbon steel surface according to the Freundlich adsorption isotherm.
- The inhibitors increase the value of activation energy of corrosion and consequently, decrease the rate of dissolution of Carbon steel in HCl solution.
- Polarization data showed that these investigated surfactant compounds acted as mixed-type inhibitors.
- The inhibition efficiencies obtained from polarization and weight loss measurements are in good agreement with each other.

- Increase of temperature leads to the increase in corrosion rate of carbon steel in HCl solution.
- Addition of KI to inhibitor formulation shows synergistic effect on corrosion inhibition efficiency of organic surfactant towards carbon steel.

ACKNOWLEDGEMENTS

Authors are grateful to the Ch. Devi Lal University, Sirsa authorities for providing the necessary infrastructural facilities to carry out the research work.

REFERENCES

1. A. A. Mazhar, W.A. Badaway and M.M. Abou-Romia, *Surf. Coat. Technol.*, 29, 335 (1986).

2. M. Stern and A.I.J. Geary, *J. Electrochem. Soc.*, 104, 56 (1957).
3. A. K. Maayta and N.A.F. Al-Rawashdeh , *Corros Sci.*, 46, 1129 (2004).
4. E. E. Ebenso ,P.C.Okafor and U. J. Ekpe, *Anti-Corrosion Methods and Materials*, 37, 381 (2003).
5. G. Bereket, A.Pinarbasi and C. Ogretir, *Anti-Corrosion Methods and Materials*, 51, 282 (2004).
6. A. S. Fouda, M. N. Moussa, F. I. Taha and A. I. Elneanaa, *Corros. Sci.*, 26, 719 (1986).
7. T. Zhao and G. Mu. *Corros. Sci.* 41,1937 (1999).
8. N. Al-Andis, E. Khamis, A.Al-Mayouf and H. Aboul-Enein, *Corros. Prev. Cont.*, 42, 13 (1995).
9. A. Kazaraji, S. Keertit, J.Aride, K.Bougrin and M.Soufiaoui, *Bull. Electrochem.*, 16 (3), 97 (2000).
10. E. E. Oguzie, *Corros. Sci.*, 49,1527 (2007).
11. M. Kliskic, J.Radosevic, S.Gudic and V. Katalinik, *J. Appl. Electrochem.*, 30, 823 (2000).
12. A.Yurt, S.Ulutas and H. Dal, *Appl.Surf.Sci.*, 253, 919 (2006).
13. S. A. Abd E L-Maksoud and A. S. Fouda, *Mater. Chem. Phys.*, 93, 84 (2005).
14. O. K. Abiola, and N.C.Oforka, *Corros. Sci. & Eng.*, 3, 21 (2002).
15. E. E. Ebenso, *Nig. Corros. J.*, 1 (1), 29 (1998).
16. B. B. Damaskin "Adsorption of organic compounds on electrodes(Plenum press) N.Y., p. 221 (1971).
17. E. E. Ebenso, *Mater.Chem.Phys.*, 79,58 (2003)
18. G. K. Gomma and M.H.Wahdan, *Mater. Chem. Phys.*, 30, 209 (1995).
19. J. Marsh "Advanced Organic Chemistry" 3rd ed., Wiley Eastern New Delhi, (1988).
20. M. S. Soliman and Ph. D. Thesis, Alex. Univ., Egypt (1995).